

# Synthesis and Properties of Novel Non-Ionic Polyurethane Dispersion Based on Hydroxylated Tung Oil and Alicyclic Isocyanates

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## Abstract

Hydroxylated Tung oil (HTO) based nonionic polyurethane dispersion (HTO-NPUD) were synthesized using dicyclohexyl methane diisocyanate (HMDI) and HTO as main hydrophobic materials whereas polyethylene glycol-800 (PEG-800) as hydrophilic chain extender. To effectively study the effects of HTO on properties of NPUD, polypropylene glycol-400(PPG-400) based NPUD was prepared by HMDI reacting with PPG-400 and PEG-800. The structures of those novel nonionic polyurethane dispersions were characterized by FTIR and <sup>1</sup>H NMR. Moreover, particle size and size distribution, cloud point and surface tension had been investigated. Results showed that, by comparing with PPG based NPUD (PPG-NPUD), the introduction of HTO into NPUD result in larger particle size and more uniformed particle size distribution, higher cloud point and lower surface tension.

## Keywords

Nonionic Polyurethane, Hydroxylated Tung Oil, Cloud Point, Surface Tension

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## 1. Introduction

Waterborne polyurethanes or polyurethane dispersions (PUDs) are a class of polymer dispersions with excellent comprehensive performance which exhibit a wide range of advantages such as low volatility of organic solvent, non-toxic, non-flammability and energy saving. It is for this reason that PUDs have been gaining thorough study and will be further developed into more environmental, biodegradable and functional materials. Among all types of PUDs, nonionic PUD (NPUD) without ion dangling on its molecular chain is provided with improved acid and alkali resistance, electrolyte sexual tolerance and can be applied in the development of synthetic leather surfactant and textile finishing agent [1]-[3].

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Tung oil [4], one of Chinese specialty, is a kind of renewable, environmentally friendly and biodegradable natural resource with attainable development. The introduction of tung oil related structure which contains 3 conjugated double bonds per fatty acid chain [5] into polyurethane can not only make it more eco-friendly but also provide potential functions such as being oxidized, hybridization with other materials or cross-link in a complex molecule. These features make it become an industrially attractive raw material for the polyurethane industry. Before preparing polyurethane, tung oil is required to be functionalized [1]. Having both triglyceride and unsaturated bond as active points, tung oil could be hydroxylated by aminolysis or alcoholysis from ester and/or by reaction at the double bond [6] [7]. HTO-based polyols prepared by the first method not only introduce hydroxy groups but also retain the active conjugated double bonds in its molecular chain. Those hydroxylated by the latter method destroy double bonds forming polyhydroxy (three or more hydroxy) compounds which are usually suitable for polyurethane foam. Moreover, the functionality of hydroxy group is hard to control.

The HTO prepared by first method (through ester) has functionality of two and can be reacted with isocyanate. This passage aims to synthesize a novel HTO-based NPUD used for macromolecule surfactant with conjugated double bonds. Compared with micromolecule surfactants, whose residues after emulsification may harm the polymer matrix, macromolecule surfactants have properties of perfect dispersity, film-forming ability, environmental friendliness, stability [8] [9] and, furthermore, the ability of forming polymer alloy by blending or crosslinking with the polymer matrix. And properties of those polymer alloys could be improved owing to the potential ability of double bond provided by tung oil. Therefore, the investigation on such HTO-NPUD broadens the application of macromolecule surfactant, lessens the cost of raw material and better the environment.

The present study aims to develop novel, biobased HTO-NPUD with post crosslinking function, based on the HTO that is hydroxylated via ester mentioned above. Firstly, NPUD was synthesized from HMDI reacting with HTO and PEG-800. Then, the structures of the NPUDs were characterized by IR and NMR, and the influence of HTO on the performance of NPUD were studied and analyzed including particle size, cloud points and surface tension. In order to make better investigation analysis for effect of HTO on PUD, PPG-NPUD was selected to compare with HTO-NPUD. The reason to use PPG-NPUD as comparison is that PPG-400 is a kind of common material in synthesis of polyurethane and provides similar molecular weight with HTO.

## 2. Experimental Section

### 2.1. Materials

Polyethylene glycol-800 (PEG-800, Bayer, Germany), polypropylene glycol-400 (PPG-400, Haian petrochemical plant, China). Reagents above were dealt with vacuum drying oven at certain temperature before use. HTO was kindly provided from US A-line Company. Dicyclohexyl methane diisocyanate (HMDI) was purchased from Wanhua Chemical Group Company. N-methyl pyrrolidone (NMP) was purchased from Shanghai Chemical Reagent Company of China Pharmaceutical Group, freed from moisture using anhydrous 4A molecular sieve. Distilled water was used as the dispersing phase.

### 2.2. Synthesis of NPUD

The recipes for NPUD are showed in **Table 1**. PEG-800, PPG-400 and NMP have been dewatered in advance.

HTO, PEG and HMDI were simultaneously added into a 500 mL four-necked flask equipped with stirrer and thermometer. The reaction was carried out in the protection of nitrogen gas and under a constant temperature at 80°C - 90°C heating with oil bath. When the NCO group content reached to a designed value, distilled water was added and the stirring rate was raised after the temperature was lowered. Then HTO-NPUD was obtained by the

**Table 1.** The basic recipes, molecular weight and cloud point of two NPUDs.

Samples	The Basic Recipes				$M_n$ (g/mol)	Cloud Point (°C)
	PPG-400	HTO	PEG-800	HMDI		
PPG-NPUD	1	0	1	2	7800	34
HTO-NPUD	0	1	1	2	8200	69

emulsification of HTO-NPU prepolymer. In this reaction process, a small amount of NMP was added to adjust the viscosity. The synthesis of PPG-NPUD was similar to that of HTO-NPUD. The synthesis process of NPUDs is showed in **Figure 1**.

### 2.3. Characterization

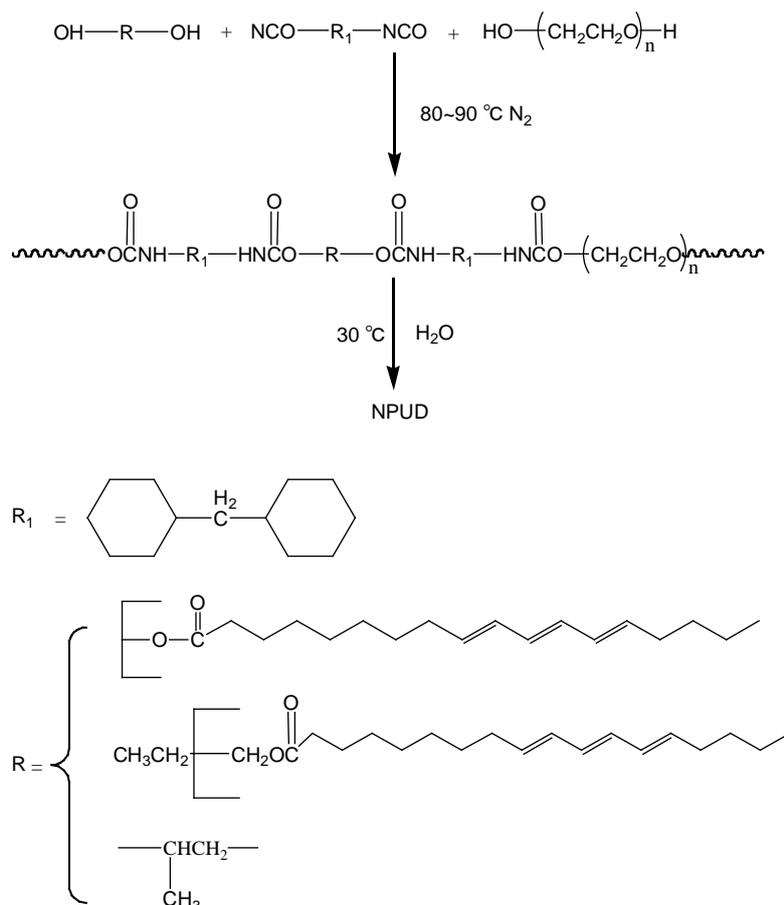
All infrared spectra of NPUDs were obtained using a SHIMADZU FTIR-8700 Spectrophotometer. The frequency range covered was from 4000 to 400  $\text{cm}^{-1}$  by averaging 16 scans at a resolution of 4  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance 400MH superconducting NMR Spectrometer using DMSO- $d_6$  as the solvent at a concentration of ~5% (w/v). All spectra were recorded at room temperature (298 K). Chemical shifts ( $\delta$ ) are given in parts per million with tetramethylsilane (TMS, 0.1%) as internal standard. Coupling constants (J) are given in Hertz.

The average particle size and distributions of NPUDs were measured with a Malvern ZEN3690 laser particle sizer (UK). The cloud points of aqueous polyurethane were measured using distilled water measurement according to GB/T5559-1993. Samples were regularly diluted to different concentrations and the surface tensions were investigated with DATAPHYSICS DCAT21 automatic interface tensiometer.

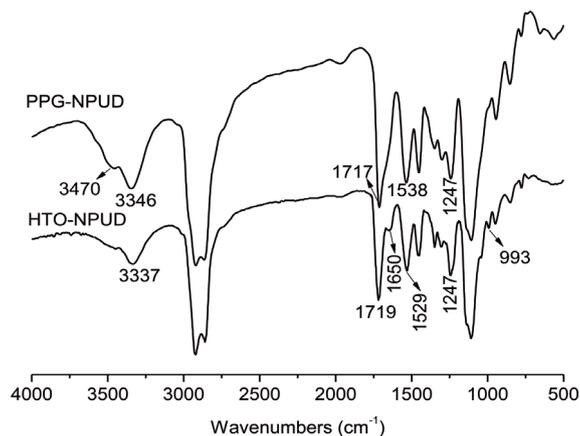
## 3. Results and Discussion

### 3.1. Characterization of Nonionic Polyurethane

The FTIR spectra of PPG-NPUD and HTO-NPUD are shown in **Figure 2**. The peaks found at 1538  $\text{cm}^{-1}$  (1529  $\text{cm}^{-1}$ ) and 1247  $\text{cm}^{-1}$  belong to Amid II and Amid III bands formed by vibrational coupling between N-H deformation vibration and C-N stretching vibration [10], respectively. Peak at 1650  $\text{cm}^{-1}$  belongs to Amid I band.



**Figure 1.** Synthesis process of NPUDs.



**Figure 2.** The FTIR spectra of PPG-NPUD and HTO-NPUD.

The absorption peak at  $1110\text{ cm}^{-1}$  are due to hydrophilic C-O-C stretching vibration. No peak at around  $2250\text{ cm}^{-1}$ , which is character peak of free NCO group, indicates that NCO in this product has totally reacted. The above characteristic spectra prove that the resultants are the expected polyurethanes. The absorption peaks of N-H at  $3346\text{ cm}^{-1}$ ,  $3337\text{ cm}^{-1}$  illustrate that N-H possibly formed hydrogen bond with C=O. And this phenomenon is proved by the fact that the absorption peaks of C=O are at  $1719\text{ cm}^{-1}$  and  $1717\text{ cm}^{-1}$  instead of  $1732\text{ cm}^{-1}$  which is the characteristic peak of free C=O. In comparison with PPG-NPUD, there is one more peak at  $993\text{ cm}^{-1}$  that represents characteristic peak of conjugated double bond in the spectrum of HTO-NPUD, suggesting that HTO is successfully introduced into NPUD structure.

The  $^1\text{H}$  NMR spectra of PPG-NPUD and HTO-NPUD are presented in **Figure 3**. The peaks at 6.80 - 7.25 ppm belong to proton NH of -NH-COO- group. Proton  $\text{CH}_2$  joined with oxygen located at 3.15 - 3.71 ppm. Peaks at 1.56 - 1.75 ppm and 0.88 - 1.75 ppm are related to proton  $\text{CH}_3$  and proton  $\text{CH}_2$ . The small peaks displayed at 5.0 - 6.5 ppm in **Figure 3(b)** are attributed to three conjugated double bonds. These evidences also prove that the synthesis of NPUD and the introduction of HTO into NPUD are successful. Moreover, both hydrophilic group and hydrophobic chain segment are proved to be introduced into NPUD.

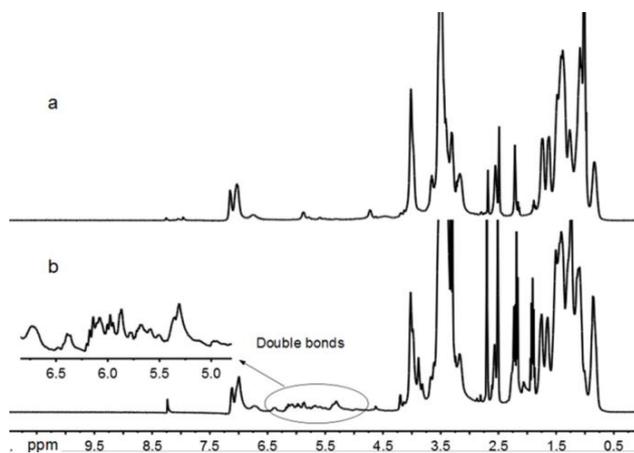
### 3.2. Particle Size and Size Distribution of NPUD

PUD is macromolecule of polyurethane dispersing in water in the form of latex particle whose diameter is particle size. Particle size and its distribution have a direct effect on the emulsion's properties such as the color, transparency and stability. The decrease in particle size will result in an increase in transparency, stability [11] and dissolution rate [12] of PUD which is a kind of milky white emulsion.

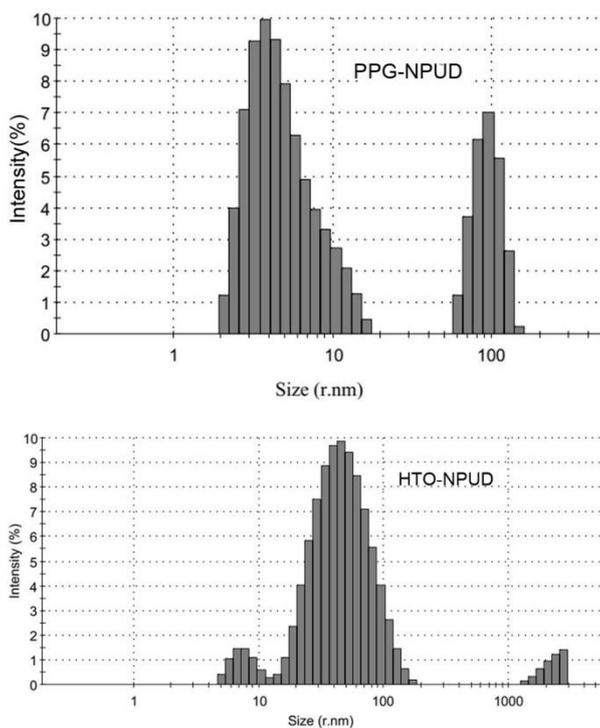
It is evident from **Figure 4** that the introduction of HTO makes a significant difference in particle size and size distribution compared with PPG-NPUD. For PPG-NPUD, most particle diameters are 2 - 10 nm, others distribute between 80 - 120 nm, indicating that the size distribution of PPG-NPUD is a multiple distribution. These two size distributions may be induced by the following reason. It is expected that the reaction of oleophilic HMDI and PPG forms oleophilic particles with large diameter. While reacting rate of HMDI and hydrophilic PEG is higher than that of HMDI and PPG, resulting in another smaller particle size. By contrast, particle size of HTO-NPUD is relatively larger and size distribution is narrower (most in 5 - 100 nm and few in 2 - 10 nm). The possible reason is that, compared with PPG-NPUD which is a linear chain polymer containing hydrophilic group, HTO was introduced into HTO-NPUD in the form of hydrophobic side chain, creating intermolecular winding then causing larger particle size. Meanwhile, the space steric hindrance of the large side chain weakens the hydrogen bonding interaction inside the NPU, balancing hydrogen bonding effect on the whole system then resulting in more uniform particle size distribution.

### 3.3. Cloud Point

The cloud point is a temperature at which a homogenous surfactant solution separates into two coexisting phases. It is basically affected by its molecular structure [13], its own concentration [14] and the presence of additives [15]. For nonionic surfactant which hydrogen bond can be formed with water, the intensity and number of



**Figure 3.** The  $^1\text{H-NMR}$  spectra of NPUD ((a): PPG-NPUD; (b): HTO-NPUD).



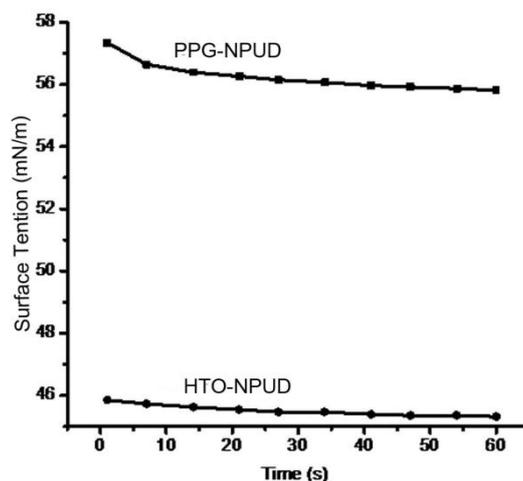
**Figure 4.** The particle sizes and distributions of PPG-NPUD and HTO-NPUD.

hydrogen bonds have profound impact on cloud point [16] as well.

As is indicated in **Table 1**, the cloud point of HTO-NPUD is much higher than that of PPG-NPUD, which shows that the introduction of HTO structure increases the cloud point of NPUD. According to the influence of HTO on particle size and size distribution of NPUD, the hydrogen bonding interaction inside the polymer is weakened, while the intensity and number of hydrogen bonds between NPUD and water are enhanced. So cloud point increases with increasing amount of energy consumed to destroy those hydrogen bonds between NPUD and water.

### 3.4. The Surface Tension

The surface tension is induced by the liquid surface shrinkage that is an important property of surfactant. **Figure 5** shows that the surface tension of HTO-NPUD (45.6 mN/m) is much lower than that of PPG-NPUD (55.8 mN/m)



**Figure 5.** The surface tension changes of PPG-NPUD and HTO-NPUD with time.

in the same conditions, which indicates that the surface tension of NPUD is significantly affected by the introduction of HTO. On the surface of NPUD aqueous emulsion, hydrophilic groups combine with water inside, while hydrophobic chains arrange outside, whose repulsion destroy the power among water molecules. So the surface tension reduction may be induced by the introduction of long oleophilic alkyl chain as side chain of HTO into NPUD.

#### 4. Conclusion

A type of novel NPUDs have been successfully synthesized by the reaction of HMDI with HTO/PPG-400 and PEG-800. HTO with three conjugated double bonds had been introduced into the NPUD. In spite of the fact that the particle size of HTO-NPUD was much larger than that of PPG-NPUD, the introduction of HTO may improve the stability of NPUD emulsion owing to the more uniformed particle size distribution. The cloud point of HTO-NPUD was remarkably higher than that of PPG-NPUD, indicating that HTO significantly improved thermal stability of NPUD. Furthermore, the surface tension of the emulsion was reduced by the introduction of hydrophobic chain from HTO. The lower surface tension suggested that HTO-NPUD had obvious surface active property and provided possibility of using HTO-NPUD as surfactant. And the three conjugated double bonds would endow more excellent performance that is worth to be further studied.

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